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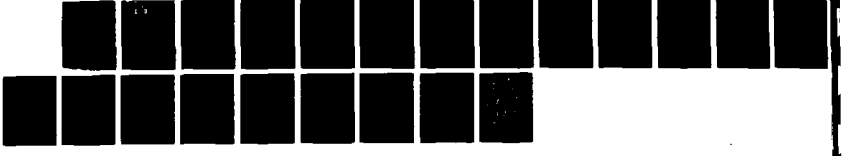

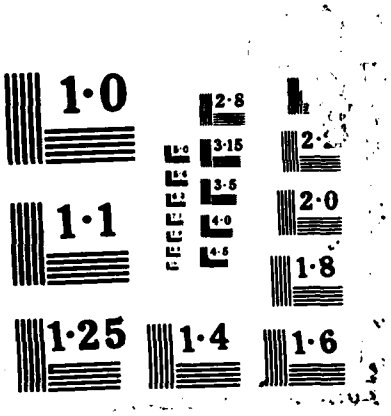
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The series of neopentylgallium compounds, $Ga(CH_2CMe_3)_3$, $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)_2Br$, $Ga(CH_2CMe_3)Cl_2$, $Ga(CH_2CMe_3)I_2$, have been prepared by very facile, high yield routes, have been easily purified and have been fully characterized. The new compound $Ga(CH_2CMe_3)_3$ is a nonpyrophoric liquid which exists as monomeric, three-coordinate gallium species in benzene solution. Cryoscopic molecular weight studies indicate that $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)Cl_2$ and $Ga(CH_2CMe_3)Br_2$ are dimeric in benzene solution. Consequently, it is noteworthy that an equimolar mixture of $[Ga(CH_2CMe_3)_2Cl]_2$ and $[Ga(CH_2CMe_3)Cl_2]_2$ does not undergo a rapid

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19. ABSTRACT (continued)

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O. T. Beachley, Jr. and J. C. Pazik

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# Synthesis and Characterization of Neopentylgallium Compounds

by

O. T. Beachley, Jr. and J. C. Pazik

## Abstract

The series of neopentylgallium compounds, $Ga(CH_2CMe_3)_3$, $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)_2Br$, $Ga(CH_2CMe_3)Cl_2$, $Ga(CH_2CMe_3)I_2$, have been prepared by very facile, high yield routes, have been easily purified and have been fully characterized. The new compound $Ga(CH_2CMe_3)_3$ is a nonpyrophoric liquid which exists as monomeric, three-coordinate gallium species in benzene solution. Cryoscopic molecular weight studies indicate that $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)Cl_2$ and $Ga(CH_2CMe_3)Br_2$ are dimeric in benzene solution. Consequently, it is noteworthy that an equimolar mixture of $[Ga(CH_2CMe_3)_2Cl]_2$ and $[Ga(CH_2CMe_3)Cl_2]_2$ does not undergo a rapid exchange reaction at room temperature as four $^1H$ NMR lines are observed. A comparison of the properties of the neopentyl- and trimethylsilylmethylgallium derivatives suggest that the neopentyl group has larger steric effects and stronger electron withdrawing properties than the corresponding trimethylsilylmethyl substituents.

## Introduction

The utiliziation of compound semiconductors for electronic and optical devices can be related to the development of epitaxial growth techniques.[1] The technique of choice for preparing compound semiconductors such as GaAs, GaP and GaSb is organometallic vapor phase epitaxy or organometallic chemical vapor deposition. Since only a surprisingly few organogallium compounds, $GaMe_3$ and $GaEt_3$, are readily available as gallium sources, our research program has been directed toward the synthesis and characterization of new organogallium compounds. In order for a gallium compound to be a useful gallium source, the compound should be readily prepared and easily purified as well as be a volatile liquid with excellent thermal stability at room temperature. In this paper, we report the synthesis and characterization of a series of organogallium compounds which incorporate the neopentyl ($CH_2CMe_3$=Np) group including $GaNp_3$, $GaNp_2Cl$, $GaNp_2Br$, $GaNpCl_2$ and $GaNpI_2$. These neopentylgallium derivatives are of chemical interest because the bulky neopentyl substituent with no β-hydrogen atoms might introduce unusual chemical properties. Furthermore, direct comparisons between corresponding neopentyl and trimethylsilylmethyl[2] derivatives might enhance our understanding of the electronic and steric effects of these organic substituents in organogallium chemistry.

## Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. All solvents were purified before use. Gallium(III) chloride was purified by sublimation under high vacuum at 70-80°C immediately prior to use. The compound $GaI_3$ was prepared from gallium

metal and iodine in refluxing toluene, a modification of the method of Tuck and Freeland.[3] Neopentyl chloride was purchased from Fairfield Chemical Co. and was distilled prior to use. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak) and sh (shoulder). The $^1H$ NMR spectra were recorded at 90MHz by using a Varian Model EM-390 spectrometer. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in $\delta$ units (ppm) and are referenced to $SiMe_4$ as $\delta$ 0.00 and benzene as $\delta$ 7.13. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver.[4]

Synthesis of $GaNp_3$. In a typical synthetic experiment, the Grignard reagent, NpMgCl, was prepared from magnesium turnings (5.802g, 238.6mmol) and freshly distilled neopentyl chloride (24.22g, 227.2mmol) in 100mL of diethyl ether. Even though the magnesium had been activated with iodine without stirring prior to the addition of the neopentyl chloride/ether solution, the reaction mixture was refluxed for 18h. Then a flask charged with 9.58g of freshly sublimed $GaCl_3$ (54.4mmol) dissolved in 250mL of dry diethyl ether was fitted with a condenser, mechanical stirrer and a pressure equalizing addition funnel. Under a cover of argon the Grignard solution was transferred to the addition funnel and was added to the $GaCl_3$ solution over a period of 20 min. After the addition was complete, the reaction mixture was stirred at room temperature for 18h. The stirrer, condenser and addition funnel were replaced by stoppers and a Teflon valve/adapter. The $Et_2O$ was then removed by vacuum distillation at room temperature. The crude

product, a $GaNp_3/Et_2O$ mixture, was isolated by vacuum distillation at 125°C into a side arm flask (cooled to -196°C) attached to the reaction flask by means of an 85° bent elbow. The distillation was continued for approximately 5h. The $Et_2O$ was then removed from the crude produce by a simple vacuum distillation at room temperature for 1h. The product was finally purified by vacuum distillation in a short path still at 55°C (0.001mm, dynamic vacuum). Pure $GaNp_3$ was obtained as a colorless, nonpyrophoric liquid (14.0g, 49.6mmol, 91.1% yield based on $GaCl_3$). $Ga(CH_2CMe_3)_3$. $^1H$ NMR ($C_6H_6$, $\delta$): 1.06 (s, 27H, $-CMe_3$) and 1.01 (s, 6H, $-CH_2-$). IR (neat liquid, $cm^{-1}$): 2950(vs), 2900(vs), 2860(vs), 2650(w), 1468(s), 1461(s), 1398(m), 1382(m), 1358(vs), 1229(s), 1132(m), 1095(m), 1031(m), 1006(s), 928(w), 909(w), 735(m), 703(m), 610(m), 591(m), 570(m), 460(sh), 450(m), 380(m), 310(m), 287(m). Anal. Calcd.: C, 63.63; H, 11.75. Found: C, 63.64; H, 11.68. Cryoscopic molecular weight, benzene solution, formula weight 283 (obsd. molality, obsd. mol. wt., association): 0.0770, 275, 0.965; 0.0610, 291, 1.03; 0.0510, 304, 1.07. Solubility: soluble in ether, THF, benzene and pentane. Trineopentylgallium(III) does not form stable 1:1 adducts with either THF or $Et_2O$.

Synthesis of $GaNp_2Cl$. Trineopentylgallium(III) (2.93g, 10.4mmol) was weighed in the dry box into a tared, screw-cap vial and 0.911g of freshly sublimed $GaCl_3$ (5.18mmol) was placed in a second tarred vial. Both compounds were dissolved in pentane and then were pipetted into a 100mL side arm flask. Each vial was rinsed several times (5-7) with fresh aliquots of pentane to ensure the quantitative transfer of the reagents. The flask was then stoppered, cooled to -196°C and then evacuated. After stirring at room temperature for 18h the slightly cloudy solution was filtered through a fine glass frit. The pentane was removed by vacuum distillation and $GaNp_2Cl$ was

obtained as a colorless solid in nearly quantitative yield (3.65g, 14.7mmol, 95.0% yield). The compound was further purified by recrystallization from pentane at -78°C. $GaNp_2Cl$. mp 70.0-71.5°C. $^1H$ NMR ($C_6H_6$, δ): 1.10 (s, 18H, $-CMe_3$) and 1.31 (s, 4H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 2718(vw), 2380(vw), 2284(vw), 1983(vw), 1736(vw), 1258(sh), 1234(vs), 1142(m), 1100(m), 1018(m), 1002(m), 932(w), 914(vw), 802(vw), 742(m), 725(vs), 704(m), 639(s), 593(w), 459(w), 450(w), 385(w), 360(sh), 298(m). Anal. Calcd.: C, 48.54; H,8.96. Found: C, 48.44; H, 9.26. Cryoscopic molecular weight, benzene solution, formula weight 247.5 (obsd. molality, obsd. mol. wt., association): 0.0799, 520, 2.10; 0.0608, 510, 2.06; 0.0458, 503, 2.03. Solubility: soluble in pentane, benzene, $Et_2O$ and THF. The compound, $GaNp_2Cl$, does not form stable 1:1 adducts with either THF or $Et_2O$.

Synthesis of $GaNp_2Br$. Reaction of 0.296g of $GaBr_3$ (0.956mmol) with 0.544g of $GaNp_3$ (1.92mmol) in pentane solution yielded 0.657g of the colorless crystalline solid, $GaNp_2Br$ (2.25mmol, 78.5% based on the initial amount of gallium). To facilitate the dissolution of $GaBr_3$ in pentane, a small amount of the pentane solution of $GaNp_3$ was added to the vial containing the $GaBr_3$. This vial was then rinsed several times to ensure the quantitative transfer of the reagents. Purification was as described for $GaNp_2Cl$.

$GaNp_2Br$. mp 68.5-70.0°C. $^1H$ NMR ($C_6H_6$, δ): 1.11 (s, 18H, $-CMe_3$) and 1.47 (s, 4H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 1360(vs), 1258(vw), 1233(s), 1140(w), 1098(w), 1015(w), 1000(m), 930(vw), 910(vw), 800(vw), 740(m), 722(s), 696(m), 635(m), 590(vw), 455(w), 383(w), 360(vw), 295(w). Anal. Calcd.: C, 41.15; H,7.60. Found: C, 40.85; H,7.45. Cryoscopic molecular weight, benzene solution, formula weight 291.9 (obsd. molality, obsd. mol.

wt., association): 0.0729, 646, 2.21; 0.0593, 650, 2.23; 0.0503, 645, 2.21. Solubility: soluble in pentane, benzene, THF and $Et_2O$.

Synthesis of $GaNpCl_2$. In a typical reaction 1.11g of freshly sublimed $GaCl_3$ (6.33mmol) was reacted in pentane with 0.897g of $GaNp_3$ (3.17mmol) to produce 1.72g of pure $GaNpCl_2$ (8.12mmol, 85.5% yield based on the initial amount of gallium). The compound can be further purified as described for $GaNp_2Cl$ or by vacuum distillation (0.001mm) in a short path still at 71°C. $GaNpCl_2$. mp 29.0-31.0°C. $^1H$ NMR ($C_6H_6$, δ): 0.91 (s, 8H, $-CMe_3$) and 1.25 (s, 2H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 3410(vw), 3355(vw), 2720(w), 2675(vw), 2400(vw), 2290(vw), 2110(vw), 2005(vw), 1970(vw), 1868(vw), 1780(vw), 1730(vw), 1550(vw), 1362(vw), 1263(m), 1233(vs), 1140(s), 1098(m), 1015(m), 1002(s), 928(vw), 910(vw), 845(m), 808(m), 729(vs), 631(s), 562(vw), 528(vw), 455(m), 397(vs), 372(vs), 252 (vs). Anal. Calcd.: C, 28.36; H, 5.24. Found: C, 28.36; H, 5.15. Cryoscopic molecular weight, benzene solution, formula weight 211.8 (obsd. molality, obsd. mol. wt., association): 0.0816, 423, 2.00; 0.0591, 422, 1.99; 0.0445, 418, 1.97. Solubility: soluble in pentane, benzene, THF and $Et_2O$. The compound, $GaNpCl_2$, formed a stable 1:1 adduct with THF.

Lewis Acidity Studies. The abilities of $GaNp_3$, $GaNp_2Cl$ and $GaNpCl_2$ to form Lewis acid-base adducts with $NMe_3$ have been investigated. In a typical experiment an excess of Lewis base was vacuum distilled onto a weighed quantity of the Lewis acid. After the resulting sample was warmed to room temperature, the excess base was removed. A mass measurement on the resulting product was used to determine the quantity of base which reacted. The mol ratio of the Lewis acid/base which reacted, the melting point of the resulting adduct and the $^1H$ NMR spectrum were used to support the formation of adducts. (Since THF was used as a solvent, the formation of adducts is

included in sections on the individual compounds.) The following observations for $NMe_3$ were made.

$Np_3GaNMe_3$: $GaNp_3/NMe_3$ mol ratio was inconclusive because the adduct appeared slightly volatile at room temperature (possibly related to dissociation). mp 100-108°C; $^1H$ NMR ($C_6H_6$, δ): 0.74 (s, 6.0 H, $CH_2$), 1.25 (s, 28.0 H, $CMe_3$), 1.73 (s, 9.0 H, $NMe_3$).

$ClNp_2GaNMe_3$: $GaNp_2Cl/NMe_3$ mol ratio (mass measurements): 1.06; mp 85.7-88.2°C; $^1H$ NMR ($C_6H_6$, δ): 0.71 (s, 4.1 H, $CH_2$), 1.34 (s, 17.2 H, $CMe_3$), 1.82 (s, 9.0 H, $NMe_3$). Resonance for methylene protons is a doublet (J = 6 Hz with a 300 MHz Bruker spectrometer).

$Cl_2NpGaNMe_3$: $GaNpCl_2/NMe_3$ mol ratio (mass measurements): 1.02; mp 61.0-70.0°C, $^1H$ NMR ($C_6H_6$, δ): 0.83 (s, 1.80 H, $CH_2$), 1.23 (s, 8.23 H, $CMe_3$), 1.82 (s, 9.0 H, $NMe_3$).

Synthesis of $GaNpI_2$. Because of the low solubility of $GaI_3$ in pentane, benzene was used as the reaction solvent. A 0.882g sample of $GaI_3$ (1.956mmol) was transferred as a solid to a 100mL side arm flask and the remaining traces of $GaI_3$ were rinsed into the flask with an aliquot of benzene. The sample of $GaNp_3$ (0.277g, 0.978mmol) was dissolved in benzene and transferred into the reaction flask as described in the synthetic procedure for $GaNp_2Cl$. After stirring for 18h at ambient temperature, the benzene was removed by vacuum distillation to yield a slightly pink, viscous liquid. The final traces of benzene were removed from the product by dissolving the sample in 25mL of pentane and then by removing all volatile components under high vacuum. This process was repeated. The final product $GaNpI_2$ (0.886g, 2.25mmol) was isolated as a slightly pink solid in 76.5% yield based on the initial amount of gallium present. An analytically pure sample as a pale pink solid was obtained by recrystallization from pentane

at -78°C. $GaNpI_2$. mp 72.0-75.0°C. $^1H$ NMR ($C_6H_6$, δ): 0.99 (s, 9H, $-CMe_3$) and 1.90 (s, 2H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 1363(s), 1262(vw), 1235(vs), 1132(m), 1092(m), 1026(m), 999(m), 928(vw), 910(vw), 833(vw), 809(vw), 743(w), 721(vs), 614(m), 452(w), 383(w), 288(m). Anal. Calcd.: C, 15.22; H, 2.81. Found: C, 15.40; H, 2.97. Solubility: soluble in benzene, pentane and THF. The compound $GaNpI_2$ forms a stable 1:1 adduct with THF.

Synthesis of $Ga(CH_2SiMe_3)_2Cl$. The synthesis of $Ga(CH_2SiMe_3)_2Cl$ was as described for the preparation of $GaNp_2Cl$. The reaction of 0.994g of $Ga(CH_2SiMe_3)_3$ (3.00mmol) with 0.265g of freshly sublimed $GaCl_3$ (1.51mmol) produced $Ga(CH_2SiMe_3)_2Cl$ in nearly quantitative yield (1.17g, 4.19mmol, 92.5% yield based on the amount of gallium used). Purification was achieved by recrystallization from pentane at -78°C. $Ga(CH_2SiMe_3)_2Cl$. mp 27-29°C. $^1H$ NMR ($C_6H_6$, δ): 0.15 (s, 18H, $-SiMe_3$) and 0.20 (s, 4H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 2952(vs), 2895(m), 1935(vw), 1868(vw), 1445(w), 1420(sh), 1414(sh), 1403(w), 1353(w), 1302(w), 1259(s), 1245(vs), 1001(s), 958(sh), 850(vs), 825(vs), 758(s), 720(s), 683(m), 622(m), 610(w), 593(m), 579(m), 560(m), 512(w), 228(s). Anal. Calcd.: C, 34.36; H, 7.93. Found: C, 33.99; H, 7.56. Cryoscopic molecular weight, benzene solution, formula weight 279.6 (obsd. molality, obsd. mol. wt., association): 0.0720, 574, 2.05; 0.0542, 570, 2.04; 0.0361, 571, 2.04. Solubility: soluble in pentane, benzene and THF.

Synthesis of $Ga(CH_2SiMe_3)Cl_2$. The procedure for the synthesis of $Ga(CH_2SiMe_3)Cl_2$ was similar to that used to prepare $GaNp_2Cl$. Addition of 0.914g of $Ga(CH_2SiMe_3)_3$ (2.76mmol) to 0.973g of freshly sublimed $GaCl_3$ (5.53mmol) in pentane solution produced 1.46g of $Ga(CH_2SiMe_3)Cl_2$ (6.39mmol, 77.2% yield based on the amount of gallium used). The colorless solid,

$Ga(CH_2SiMe_3)Cl_2$, was purified by recrystallization from pentane at -40°C. $Ga(CH_2SiMe_3)Cl_2$. mp 55.0-56.8°C (lit. 48.0-49.0°C).[2] $^1H$ NMR ($C_6H_6$, δ): 0.01 (s, 9, $SiMe_3$) and 0.14 (s, 2H, $-CH_2-$). IR (Nujol mull, $cm^{-1}$): 3790(vw), 3725(vw), 3660(vw), 3498(vw), 2725(w), 2680(w), 2485(vw), 2360(vw), 2100(vw), 2035(vw), 2000(vw), 1945(w), 1875(w), 1810(vw), 1740(vw), 1648(vw), 1578(vw), 1405(s), 1345(vs), 1323(m), 1247(vs), 1020(vs), 1009(vs), 973(m), 837(vs, br), 787(s), 755(vs, br), 720(vs), 688(vs), 662(w), 621(s), 598(vs), 558(vs), 480(vw), 463(w), 380(vs), 350(vs), 298(vs). Anal. Calcd.: C, 21.09; H, 4.87. Found: C, 21.27; H, 5.01. Solubility: soluble in benzene and pentane.

## Results and Discussion

A series of neopentylgallium compounds including $GaNp_3$, $GaNp_2Cl$, $GaNp_2Br$, $GaNpCl_2$ and $GaNpI_2$ have been prepared by very facile, high yield routes, have been easily purified and have been fully characterized. The properties of these neopentyl compounds have also been compared with the corresponding trimethylsilylmethyl derivatives. In cases in which the previously reported properties of trimethylsilylmethylgallium derivatives[2] were inconsistent with those of the corresponding neopentyl derivative, the synthesis and characterization of the trimethylsilylmethylgallium derivative was reinvestigated. The characterization data for the neopentyl derivatives and the reinvestigated trimethylsilylmethyl derivatives included physical properties, elemental analyses, cryoscopic molecular weight measurements, Lewis acid-base studies and infrared and NMR spectra.

Trineopentylgallium(III) has been prepared from $GaCl_3$ by a typical Grignard reaction in diethylether solution and has been readily isolated by vacuum distillation at 55°C. For the synthetic reaction to be successful a 25% calculated excess of the Grignard reagent over $GaCl_3$, assuming complete reaction, was required. Our experimental data suggested that the reaction between the neopentyl chloride and magnesium proceeded to only 75% completion. It is of interest that $GaNp_3$ is a nonpyrophoric, colorless liquid. In comparison, $Ga(CH_2SiMe_3)_3$[2] and most other gallium alkyls[5] are pyrophoric liquids. Molecular weight studies suggest that $GaNp_3$ exists as monomeric species in benzene solution. In Lewis acidity studies, neither of the oxygen bases $Et_2O$ nor THF formed stable 1:1 adducts with $GaNp_3$, whereas THF formed an adduct with $Ga(CH_2SiMe_3)_3$. It is also noteworthy that the stronger base $NMe_3$ forms an apparent adduct with $Ga(CH_2SiMe_3)_3$ and probably with $GaNp_3$. These observations suggest that the neopentyl group

has significantly greater steric effects than does the trimethylsilylmethyl group. Alternatively, electronic effects may be responsible for the increased Lewis acidity of $Ga(CH_2SiMe_3)_3$. However, the results of our studies in organoaluminum chemistry[6] suggest that the neopentyl group has stronger electron withdrawing properties and larger steric effects than the trimethylsilylmethyl group.

The neopentylgallium(III) halides $GaNp_2X$ (X=Cl, Br) and $GaNpY_2$ (Y=Cl, I) have been prepared by stoichiometric ligand redistribution reactions between $GaNp_3$ and the appropriate gallium(III) halide. The ligand redistribution reaction has proven to be a convenient method for preparing the neopentylgallium(III) halide compounds provided that stoichiometric quantities of reagents are employed. Excess quantities of either $GaNp_3$ or the gallium(III) halide will result in the formation of additional inseparable products. Pentane is the solvent of choice for the ligand redistribution reactions involving $GaX_3$ (X=Cl, Br). These gallium halides are soluble in pentane and pentane is easily removed from the nonvolatile reaction products. In contrast, $GaI_3$ is insoluble in pentane. Therefore, $GaNpI_2$ was prepared from $GaNp_3$ and $GaI_3$ in a 1:2 mol stoichiometry in benzene solution.

The neopentylgallium(III) halides have been fully characterized. The compounds $GaNpCl_2$, $GaNp_2Cl$ and $GaNp_2Br$ are colorless solids whereas $GaNpI_2$ is a light pink solid at room temperature. Neopentylgallium(III) dichloride has a low melting point (29.0-31.0°C). Since the melting point is only slightly above room temperature, the compound has been observed to exist as either a crystalline solid, a liquid or more commonly a sticky solid. In order to minimize the problems associated with handling a sticky solid, samples of $GaNpCl_2$ were heated to form a mobile liquid prior to entry into

the dry box. It is of experimental importance that heated samples remained liquid for a reasonable length of time, about one hour or more, before crystallization. Cryoscopic molecular weight measurements indicate that the neopentylgallium(III) halide compounds ($GaNp_2Cl$, $GaNp_2Br$ and $GaNpCl_2$) are dimeric in benzene solution. The most likely structure for a dimeric molecule of this type would involve halogen donor-acceptor bridge bonds. The apparent existence of halogen bridge bonds in solution suggests that the gallium atom is not sufficiently hindered by the bulky neopentyl groups to preclude dimer formation. The dimeric nature of $GaNp_2Cl$ in solution indicates it is not as weak a Lewis acid as $Ga(C_5Me_5)_2Cl$, a molecule which is dimeric in the solid state but apparently monomeric in solution.[7] Our studies indicate that $GaNp_2Cl$ is a relatively weak Lewis acid. The compound forms a stable 1:1 adduct with $NMe_3$ but not with THF, a slightly weaker Lewis base. The only other gallium compounds which do not form stable adducts with THF are $GaMes_3$ (Mes=mesityl),[8] $Ga(C_5Me_5)_2Cl$[7] and $Ga(C_5Me_5)_3$.[9] The dihalide derivative, $GaNpCl_2$, is a stronger Lewis acid than $GaNp_2Cl$ and forms stable 1:1 adducts with both $NMe_3$ and THF. The iodide derivative, $GaNpI_2$, also forms a 1:1 adduct with THF.

The halide derivatives, $GaNp_2X$ (X=Cl, Br) and $GaNpY_2$ (Y=Cl, I) exhibit characteristic $^1H$ NMR spectra in benzene solution with the resonances for the methylene protons being downfield of that for the methyl protons for a given compound. Similar observations of the relative chemical shifts of methylene and methyl protons have been reported for benzene solutions of the (trimethylsilyl)methyl halogen derivatives of gallium and indium[10] but not for the (trimethylsilyl)methyl[11] or neopentyl[6] derivatives of aluminum. Other gallium halogen compounds which have methylene and methyl protons in a given substituent also exhibit other patterns. For example, the $^1H$ NMR

spectrum of $Ga(i\text{-}Bu)_2Cl$ (neat with sufficient benzene or $CH_2Cl_2$ for reference)[12] exhibited only one resonance; the lines for the both types of protons were coincident, whereas the line for the methylene protons of $GaEt_2Cl$ ($CCl_4$ with TMS as reference)[13] was upfield of that for the methyl line. The significance of these observations is uncertain and will be investigated further as more examples of these types of compounds are characterized.

The $^1H$ NMR spectrum of a mixture of $GaNp_2Cl$ and $GaNpCl_2$ in benzene exhibited four resonances at 1.33, 1.23, 0.99 and 0.95 ppm for the four different types of protons in the two molecules. The lines at 1.33 and 0.99ppm are assigned to the methylene and methyl groups of $GaNp_2Cl$, respectively, whereas the lines at 1.23 and 0.95ppm are assigned to the methylene and methyl groups, respectively, of $GaNpCl_2$. Although the resonances for the protons of the methyl groups are shifted upfield relative to their positions in the spectra of the pure compounds, the chemical shift of the methylene protons are in excellent agreement with those observed in the spectra of pure $GaNp_2Cl$ and $GaNpCl_2$.

The observation that bisneopentylgallium(III) chloride existed as simple dimer in solution prompted a reinvestigation of the synthesis and properties of the (trimethylsilyl)methylgallium(III) chlorides, $Ga(CH_2SiMe_3)_nCl_{3-n}$ (n=1, 2). The monochloro derivative, $Ga(CH_2SiMe_3)_2Cl$, was of particular interest because it had been reported to be a high melting, insoluble solid with a possibly polymeric structure.[2] In our current studies, $Ga(CH_2SiMe_3)_2Cl$ has been prepared in 92.5% yield as a colorless, crystalline solid from the reaction of $Ga(CH_2SiMe_3)_3$ and $GaCl_3$ in a 2:1 mol ratio. An analytically pure sample of $Ga(CH_2SiMe_3)_2Cl$ had a low melting point, 27-29°C. Like $GaNpCl_2$, $Ga(CH_2SiMe_3)_2Cl$ is best handled as a

liquid. In fact, all the properties of $Ga(CH_2SiMe_3)_2Cl$ are quite similar to those of $GaNp_2Cl$. Bis[(trimethylsilyl)methyl]gallium(III) chloride is very soluble in pentane, benzene and THF. Cryoscopic molecular weight measurements indicate that $Ga(CH_2SiMe_3)_2Cl$ is dimeric in benzene solution over a concentration range of 0.0730m to 0.0361m. The $^1H$ NMR spectrum exhibits two resonances at 0.15 and 0.20ppm for the methyl and methylene protons, respectively. The material previously reported to be $Ga(CH_2SiMe_3)_2Cl$ was prepared in approximately 50% yield by a elimination reaction between $Ga(CH_2SiMe_3)_3$ and anhydrous HCl.[2] The product was reported to exhibit a high melting point (159.5-160.0°C) and to be insoluble in pentane and benzene.[2] In addition to the discrepencies between the melting points and solubility data, the IR spectroscopic data for the two independently prepared samples are also in disagreement. Therefore, it is likely that the previous synthesis[2] did not yield $Ga(CH_2SiMe_3)_2Cl$ but perhaps some air-oxidized or hydrolyzed product.

The synthesis and characterization of (trimethylsilyl)-methylgallium(III) dichloride, $Ga(CH_2SiMe_3)Cl_2$, has also been reinvestigated. The compound was previously isolated from a ligand redistribution reaction between $Ga(CH_2SiMe_3)_3$ and $GaCl_3$ in a 1:2 mol ratio in benzene solution.[2] In the current study, $Ga(CH_2SiMe_3)Cl_2$ has also been independently synthesized by the stoichiometric ligand redistribution reaction as a colorless solid in 77.2% yield. It is noteworthy that the melting point of the crude product (48.5-51.5°C) corresponds to the value previously reported[2] for the purified compound (48-49°C). Upon recrystallization of the crude product from a pentane solution at -40°C, an analytically pure sample of $Ga(CH_2SiMe_3)Cl_2$ had a melting point of 55.0-56.8°C. The IR spectrum of an analytically pure sample of $Ga(CH_2SiMe_3)Cl_2$

did not coincide with that previously reported.[2] The earlier spectroscopic data would be in doubt if it were based on an impure sample of $Ga(CH_2SiMe_3)Cl_2$.

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